

**Appl. No. 09/945,393**

**REMARKS**

Claims 1-7, 20-27, 35-38, and 45-56 are pending in the application with claims 1, 6, 35, 36, 53, and 55 amended herein.

Page 2 of the Office Action alleges that claims 55 and 56 are directed to an invention that is independent or distinct from the invention originally claimed and withdraws such claims from consideration. Applicant traverses.

Page 2 of the Office Action states that the device set forth in claims 55 and 56 can be produced by another materially differently process in comparison to the constructively elected invention. For example, the Office Action states that "the claims 55 and 56 inventions may be produced by CVD using mixed source gases." Applicant notes that independent claim 55 expressly states that the enhanced dielectric material includes alternated, atomic layer deposited monolayers of a first dielectric material and a second dielectric material. Those of ordinary skill recognize that "CVD using mixed source gases" is incapable of forming alternated, atomic layer deposited monolayers of a first dielectric material consisting of tantalum and oxygen and a second dielectric material consisting of zirconium and oxygen, as set forth in claim 55. Accordingly, the Office Action does not identify another valid process that is materially different from the claimed inventions and is capable of producing the dielectric material of claim 55.

Further, Applicant notes that dielectric claims 36 and 45 are entitled to consideration together with respective method claims 1 and 20, as is revealed by comparison of the limitations of such claims. Similarly, Applicant notes that dielectric claim 55 is entitled to consideration along with method claim 53, as is revealed from comparison of the limitations of such claims. At least for the reasons described herein, Applicant requests consideration of claims 55 and 56 in the next Office Action.

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Claims 1-7, 20-27, 35-38, and 42-54 stand rejected under 35 U.S.C. 103(a) as being unpatentable over Raaijmakers. Applicant requests reconsideration.

Amended claim 1 sets forth a dielectric material forming method that includes, among other features, forming a second monolayer on a first monolayer and forming a dielectric layer containing the first and second monolayers. One of the first and second monolayers contains tantalum and oxygen and the other of the first and second monolayers contains oxygen and zirconium. The dielectric layer exhibits a dielectric constant greater than the first monolayer and second monolayer with 2-20% of the dielectric layer being oxygen and zirconium that is provided as in the other of the first and second monolayers. Page 3 of the Office Action incorporates by reference page 2 of the Office Action mailed June 29, 2004 and alleges that Raaijmakers suggests every limitation of claim 1 even though Raaijmakers fails disclose every limitation. Applicant traverses.

Applicant asserts that the amendment to claim 1 regarding dielectric constant is supported at least by paragraphs 24 and 45. Paragraph 24 states that tantalum pentoxide may be doped with zirconium oxide to "significantly enhance the dielectric constant." Paragraph 45 provides an example of a 50/50 combination of tantalum pentoxide and zirconium oxide monolayers that exhibited a dielectric constant of 60. The dielectric constant obtained significantly enhances the dielectric constant for tantalum pentoxide of about 26 and for zirconium oxide of about 25. Notably, pursuant to paragraph 35 of the present specification, the significantly enhanced dielectric constant was obtained even though the composition was outside the most advantageous ranges.

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Review of Raaijmakers, in particular the various paragraphs relied upon in the Office Action and in the Office Action mailed June 29, 2004, does not reveal any disclosure or suggestion to combine monolayers containing oxygen and zirconium with monolayers containing tantalum and oxygen, as claimed. Also, the Office Actions do not make any express allegation that such a teaching exists. Applicant acknowledges the discussion in paragraph 41 of Raaijmakers regarding combinations of various materials in nanolaminate dielectrics. However, the list notably does not include combinations of tantalum oxide and zirconium oxide. The Office Actions also rely upon paragraphs 72-75, 106, 123, and 124 as exemplifying formation of tantalum oxide and zirconium oxide, but the relied upon text does not contain any suggestion of combining monolayers containing oxygen and zirconium with monolayers containing tantalum and oxygen, as claimed.

Claim 1 further sets forth forming a dielectric layer with 2-20% of the dielectric layer being oxygen and zirconium that is provided as in the monolayer containing oxygen and zirconium. Regardless of the discussion in paragraph 69 of Raaijmakers regarding ratios of different metals, the discussion in paragraph 117 of slight doping effects, and the discussion in paragraph 127 of enhanced dielectric properties for nonolaminates, the Office Actions fail to disclose or suggest the claimed composition range.

First, none of the relied upon discussions in Raaijmakers are indicated to pertain to monolayers of oxygen and zirconium combined with monolayers of tantalum and oxygen, as claimed. Each of the relied upon discussions pertain to other materials and no basis exists for assuming that the same composition ranges apply to the claimed oxygen and zirconium combination with tantalum and oxygen. Applicant's assertion is

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especially pertinent given the unpredictable nature of the chemical arts. Those of ordinary skill would not expect the relied upon text in Raaijmakers to apply necessarily to the subject matter of claim 1.

Second, none of the relied upon discussions in Raaijmakers disclose a composition that is within the claimed range of 2-20%. Paragraph 69 of Raaijmakers discusses a 1:1 to 3:1 range of ratios, paragraph 17 merely mentions "slight" doping without describing a numerical range, and paragraph 127 does not provide any discussion of composition range. Accordingly, Raaijmakers clearly fails to disclose or suggest the every limitation of claim 1.

Raaijmakers exhibits clear deficiencies and the Office Actions fail to cite any relied upon text expressly disclosing or suggesting the limitations of claim 1. Nevertheless, the Office Actions state that one of the aims in Raaijmakers is to produce dielectric stacks with enhanced dielectric properties and that it would lead to "the recited amounts of metal oxides in the dielectric stack produced." Applicant asserts that the mere fact that the prior art can be modified does not make the modification obvious "unless the prior art suggested the desirability of the modification." In re Gordon, 733 F.2d 900, 221 USPQ 1125 (Fed. Cir. 1984). The Office Action does not identify any motivation disclosed in Raaijmakers to combine zirconium oxide with tantalum oxide. Even though a variety of material combinations are described in Raaijmakers, none of the combinations include zirconium oxide/tantalum oxide and Raaijmakers does not include any motivation that would prompt those of ordinary skill to attempt combination of zirconium oxide and tantalum oxide instead of those combinations listed.

The test for establishing an implicit teaching, motivation, or suggestion is what the combination of statements in a reference would have suggested to those of ordinary

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skill in the art. In re Kotzab, 217 F.3d 1365, 1371, 55 USPQ2d 1313, 1317 (Fed. Cir. 2000). The statements themselves cannot be viewed in the abstract. Id. Rather, the statements must be considered in the context of the teaching of the entire reference. Id. Further, a rejection cannot be predicated upon the mere identification in the reference of individual components of claimed limitations. Id. "Rather, particular findings must be made as to the reason the skilled artisan, with no knowledge of the claimed invention, would have selected these components for combination in the manner claimed." Id. Applicant asserts that the Office Action and Raaijmakers lack the required "particular findings." Even though the Office's obviousness rejection is based upon a single prior art reference, there must be a showing of a suggestion or motivation to modify the teachings of that reference. Id. Accordingly, given the deficiencies of the Raaijmakers and the Office Action, Applicant asserts that the Office's findings are not supported by substantial evidence. Applicant asserts that claim 1 is patentable over Raaijmakers.

Claims 2-7 and 51 depend from claim 1 and are patentable at least for such reason as well as for the additional limitations of such claims not disclosed or suggested. For example, claim 6 sets forth that forming of the dielectric layer includes annealing. In the present specification, [0038] sets forth that annealing is one example of additional processing that can advantageously distribute components originally formed as a discrete layer throughout a composite dielectric material such that substantial homogeneity is achieved. Applicant acknowledges a discussion in [0099] and [0105] of Raaijmakers regarding annealing amorphous TaO<sub>2</sub> dielectric layers. However, such annealing only occurs when a crystallized dielectric is desired. Accordingly, Applicant asserts that Raaijmakers does not disclose annealing a dielectric

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material having the monolayers and composition set forth in claim 1. Also, claim 51 sets forth that 5-15% of the dielectric layer is the other of the first and second monolayers containing zirconium and oxygen. Since Raaijmakers fails to disclose or suggest the compositional range set forth in claim 51.

Claim 20 sets forth a dielectric material forming method that includes, among other features, chemisorbing alternated monolayers of a first dielectric material and a second dielectric material over a substrate and providing fewer monolayers of the second material compared to the first material. The first material contains tantalum and oxygen and the second material contains zirconium and oxygen with 2-20% of the monolayers being monolayers of the second material. As discussed above with regard to the deficiencies of Raaijmakers as applied to claim 1, such reference fails to disclose or suggest 2-20% of the monolayers being monolayers of the second material containing zirconium and oxygen, as set forth in claim 20. At least for such reason, Raaijmakers fails to disclose or suggest every limitation of claim 20.

Claims 21-27 depend from claim 20 and are patentable over Raaijmakers at least for such reason as well as for the additional limitations of such claims not disclosed or suggested. For example, claim 21 sets forth that from about 5% to about 15% of the monolayers are second material monolayers. Also, claim 27 sets forth that the method of claim 20 further includes annealing the monolayers. As will be appreciated from the above discussion regarding the deficiencies of Raaijmakers as applied to respective claims 51 and 6, such reference fails to disclose or suggest the subject matter of claims 21 and 27.

Amended claim 35 sets forth a dielectric material forming method that includes ALD of a plurality of monolayers, each of the plurality of monolayers containing both

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zirconium oxide and tantalum oxide, and forming a dielectric material. The dielectric material exhibits a dielectric constant greater than that of tantalum oxide and zirconium oxide. Review of Raaijmakers reveals that such reference fails to disclose or suggest a monolayer or plurality of monolayers each containing both zirconium oxide and tantalum oxide. Raaijmakers also fails to disclose or suggest a dielectric material containing such monolayers exhibiting a dielectric constant greater than that of tantalum oxide and zirconium oxide.

None of the paragraphs relied upon in the Office Action or those paragraphs associated with Figs. 5 and 6, describing various reaction chemistries, disclose or suggest a monolayer of mixed metal oxide composition. Applicant notes that the Office Actions do not apparently address the specific limitations of claim 35 where each monolayer includes both an oxide of zirconium and tantalum oxide. At least for such reason, Raaijmakers fails to disclose or suggest every limitation of claim 35. In addition, as will be appreciated from the above discussion regarding the deficiencies of Raaijmakers as applied to claim 1, such reference fails to disclose or suggest combining zirconium oxide and tantalum oxide to enhance the dielectric constant of tantalum oxide.

Amended claim 36 sets forth a dielectric layer that includes, among other features, a first monolayer containing tantalum and oxygen and a second monolayer containing zirconium and oxygen with 2-20% of the dielectric layer being oxygen and zirconium that is provided as in the second monolayer. The dielectric layer exhibits a dielectric constant greater than the first monolayer and second monolayer. As may be appreciated from the above discussion regarding the deficiencies of Raaijmakers as applied to claim 1, such reference fails to disclose or suggest 2-20% of the dielectric

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layer being oxygen and zirconium as well as the dielectric layer exhibiting a dielectric constant greater than the first monolayer containing tantalum and oxygen and the second monolayer containing oxygen and zirconium. Claims 37, 38 and 52 depend from claim 36 and are patentable at least for such reason as well as for the additional limitations of such claims not disclosed or suggested.

Claim 45 sets forth an enhanced dielectric material that includes, among other features, alternated chemisorbed monolayers of a first dielectric material and a second dielectric material over a substrate. The enhanced dielectric material contains fewer monolayers of the second material compared to the first material with 2-20% of the monolayers being monolayers of the second material. The first material contains tantalum and oxygen and the second material contains zirconium and oxygen. As may be appreciated from the above discussion regarding the deficiencies of Raaijmakers as applied to claim 20, such reference fails to disclose or suggest 2-20% of the monolayers being monolayers of the second material containing zirconium and oxygen. Claims 46-50 depend from claim 45 and are patentable at least for such reason as well as for the additional limitations of such claims not disclosed or suggested.

As may be appreciated from the above discussions regarding the deficiencies of Raaijmakers as applied to claims 1, 20, and 27, Applicant asserts that claims 53 and 54 are also patentable over Raaijmakers. Claims 55 and 56 are patentable at least for the reasons discussed above regarding claims 1 and 20. In addition, claims 53 and 55 set forth that the dielectric material exhibits less current leakage than the first material. Raaijmakers fails to appreciate this advantage of combining monolayers containing tantalum and oxygen with monolayers containing zirconium and oxygen. Raaijmakers discusses leakage current improvements, for example, in paragraph 11 and elsewhere,



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but in each instance resolution of the problem involves increasing dielectric thickness. Raaijmakers does not disclose or suggest improvement in the intrinsic leakage current properties.

Applicant herein establishes adequate reasons supporting allowance of claims 1-7, 20-27, 35-38, and 45-56 and requests allowance of all such pending claims in the next Office Action.

Along with an Office Action response filed Dec. 3, 2003, Applicant previously provided a copy of a Form PTO-1449 originally submitted on Nov. 29, 2001 along with a copy of a reference apparently missing from the Office's file. The subject Gan et al reference was not considered most recently as apparently still missing from the Office's file. Applicant notes that Gan et al is included in the Office's image file wrapper for the present application as an attachment to the Remarks filed Dec. 3, 2003. Included herewith please find another copy for the Examiner's convenience. Applicant requests consideration of the reference and return of the initialed Form PTO-1449 with the next Office Action.

Respectfully submitted,

Dated: 25 Apr 2005

By: \_\_\_\_\_

  
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# Dielectric property of $(\text{TiO}_2)_x-(\text{Ta}_2\text{O}_5)_{1-x}$ thin film.

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$(\text{TiO}_2)_x-(\text{Ta}_2\text{O}_5)_{1-x}$  thin films were prepared with radio-frequency magnetron sputtering deposition in this study. The dielectric constant measured from these films appears to critically depend on the amount of  $\text{TiO}_2$  incorporated into the film and post-anneal condition. The composition dependence was found similar to that reported on  $(\text{TiO}_2)_x-(\text{Ta}_2\text{O}_5)_{1-x}$  bulk. The highest value of dielectric constant is about 55 for a  $\text{TiO}_2$  content of 8% and annealing at 800 °C. Compared to pure  $\text{Ta}_2\text{O}_5$  thin films, significant enhancement in dielectric constant is obtained by adding small quantity of  $\text{TiO}_2$ . © 1998 American Institute of Physics. [S0003-6951(97)02841-6]

Recently, Cava *et al.*<sup>1</sup> have reported that the dielectric constant of tantalum oxide ( $\text{Ta}_2\text{O}_5$ ) can increase from 35.4 to 126.2 by adding about 8 mol % of titanium oxide ( $\text{TiO}_2$ ).  $\text{Ta}_2\text{O}_5$  has been studied intensively as the dielectric for the next generation high density electronic memories because of its higher dielectric constant as compared with the oxide/nitride/oxide stack currently used.<sup>2-7</sup> In addition, both  $\text{TiO}_2$  and  $\text{Ta}_2\text{O}_5$  films can be fabricated with chemical vapor deposition (CVD) which is a common technique used in the current integrated circuit (IC) fabrication.<sup>8</sup> In consequence, their results appear to be very attractive since further improvement on the dielectric constant would extend  $\text{Ta}_2\text{O}_5$  application in electronic memory to even higher density.

Their measurements were carried out on the  $(\text{TiO}_2)_x-(\text{Ta}_2\text{O}_5)_{1-x}$  bulks that were prepared with a standard ceramic processing technique. The processing temperature is 1400 °C; that is well above the allowed temperature for current IC processing. As a result, it is important to examine if the same properties can be reproduced from thin  $(\text{TiO}_2)_x-(\text{Ta}_2\text{O}_5)_{1-x}$  film that are fabricated at lower temperature.

In this letter, we show that similar composition dependence of dielectric constant is observed in thin  $(\text{TiO}_2)_x-(\text{Ta}_2\text{O}_5)_{1-x}$  films. Significant increase of dielectric constant is also found when the films are crystallized during post-anneal. Nevertheless, the highest dielectric constant measured in this work is about 55; that is much less than the value reported on bulks.

Figure 1 is the schematic drawing of the capacitor fabricated in this study. The substrate was a thermally oxidized Si wafer deposited with Pt (~1500 Å) that serves as a bottom electrode.  $(\text{TiO}_2)_x-(\text{Ta}_2\text{O}_5)_{1-x}$  films were deposited with an rf magnetron sputtering system. Targets used in the deposition were made with various compositions of  $\text{Ta}_2\text{O}_5$  and  $\text{TiO}_2$  powders that were mixed homogeneously and fired at 1000 °C for 2 h. The deposition was carried out at 200 °C and in the oxygen-containing ambient to suppress oxygen deficiency of the deposited films as much as possible. Film thickness was kept around 1100 Å of which the exact value depends on the film composition. The composition of targets and films were examined primarily with energy dispersive spectrometer (EDS) of which accuracy has been calibrated against wavelength dispersive spectrometer (WDS). Capacitance

measured with HP 4284A was carried out at zero bias and 1 MHz.

Figure 2 shows the film composition as the function of target's, both are expressed in mole fraction of  $\text{TiO}_2$ . From the result of linear fit, the line in the figure, it appears that composition of films's and target's is pretty close to each other, the slope of fit is  $1.00 \pm 0.03$ . The larger deviation found in the high  $\text{TiO}_2$  fraction case is not clear, possibly caused by competing incorporation between Ti and Ta during deposition. The fit also helps in determining the composition of film prepared from the target with a 1%  $\text{TiO}_2$  addition since it is hardly detectable in EDS and WDS. Film's composition is summarized in Table I with other results.

Figure 3 is the dielectric constant plotted with the mole fraction of  $\text{TiO}_2$ . The typical film thickness of  $(\text{TiO}_2)_x-(\text{Ta}_2\text{O}_5)_{1-x}$  is around 1100 Å. Two sets of results are shown in the figure; one is measured from the as-deposited films, the other is obtained from the films being annealed at 800 °C for 1 h in  $\text{N}_2$  ambient. In either case, the dielectric constant strongly depends on the amount of  $\text{TiO}_2$ . It first increases with the addition of  $\text{TiO}_2$ , then drops sharply as the fraction of  $\text{TiO}_2$  continues to increase. The highest dielectric constant in both cases appears at the same fraction of  $\text{TiO}_2$ ; i.e., around 8% of incorporation. This is in agreement with what was observed in bulk  $(\text{TiO}_2)_x-(\text{Ta}_2\text{O}_5)_{1-x}$ . It is also noted that high-temperature anneal seems to enhance the dielectric constant for all compositions. For example, the dielectric constant of

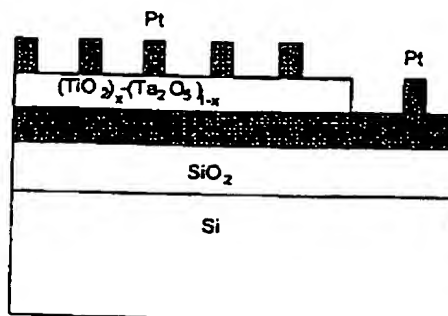


FIG. 1. The schematic drawing of  $(\text{TiO}_2)_x-(\text{Ta}_2\text{O}_5)_{1-x}$  capacitors.

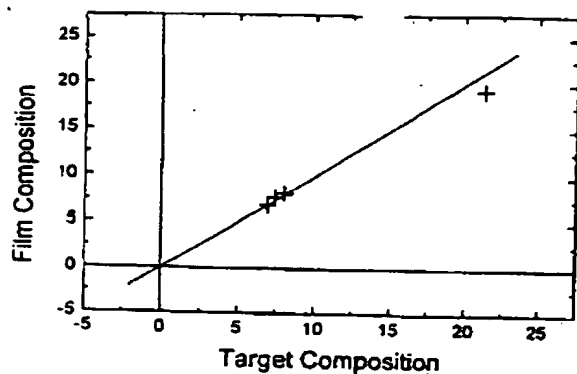


FIG. 2. Film composition as a function of target composition. Both axes are expressed in mole fraction of  $\text{TiO}_2$ .

$(\text{TiO}_2)_{0.08}-(\text{Ta}_2\text{O}_5)_{0.92}$  films has increased from 30 to 55 after an 800 °C anneal.

The crystalline phases of all films have been examined with a conventional x-ray diffractometer. Figure 4 is the result of x-ray diffraction of  $(\text{TiO}_2)_{0.08}-(\text{Ta}_2\text{O}_5)_{0.92}$  films that were annealed under various conditions. The films under examination are of the same thickness (1100 Å) and were being deposited on the same bottom Pt electrode. Except for the as-deposited films, all were heat treated for 1 h under the specified temperature. Apparently, the film remains amorphous for the annealing temperature below 600 °C. For temperature higher than 800 °C, the crystalline structure starts to form and was identified to be the metastable  $H'$  monoclinic phase which is believed to be the same phase observed on bulk  $(\text{TiO}_2)_{0.08}-(\text{Ta}_2\text{O}_5)_{0.92}$ .

It is found that the dielectric constant critically depends on whether the crystalline phase has formed. Figure 5 is the dielectric constant of  $(\text{TiO}_2)_{0.08}-(\text{Ta}_2\text{O}_5)_{0.92}$  films plotted as the function of annealing temperature. The film thickness was measured to be 1100 Å, and the capacitance measurement was still carried out under zero bias and at 1 MHz. As shown in the figure, the dielectric constant remains low and unchanged for the as-deposited and 600 °C annealed films. However, the dielectric constant shoots up as the annealing temperature is over 800 °C which is exactly the crystallization temperature being detected from x-ray diffraction. Once the crystalline phase has appeared, the dielectric constant is again relatively independent of the annealing temperature.

Table I lists the dielectric constant from bulk<sup>1</sup> and film (annealed at 800 °C) of the same composition. Note that some of bulk results were obtained with interpolation which may not be exact but would not be too far off either. Evidently, the dielectric constant measured from films is significantly less than that of bulk's except for the case for 1%

TABLE I. The dielectric constant of  $(\text{TiO}_2)_x-(\text{Ta}_2\text{O}_5)_{1-x}$  bulks and films.

$x =$	0.01	0.07	0.08	0.082	0.193
film <sup>a</sup>	40.6	50.9	54.7	45.1	33.4
bulk <sup>b</sup>	27.8	108.5	126.2	123.6	60.8
film/bulk ratio	1.46	0.47	0.43	0.36	0.55

<sup>a</sup>Annealed at 800 °C.

<sup>b</sup>Interpolated from Ref. 1.

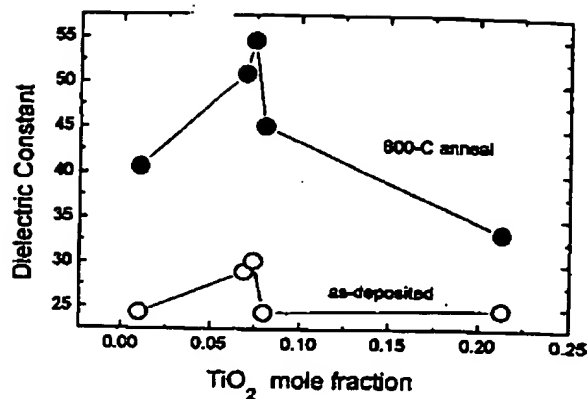


FIG. 3. Dielectric constant as a function of  $\text{TiO}_2$  incorporation. The measurement was performed at zero bias and 1 MHz with dielectric film thickness around 1100 Å.

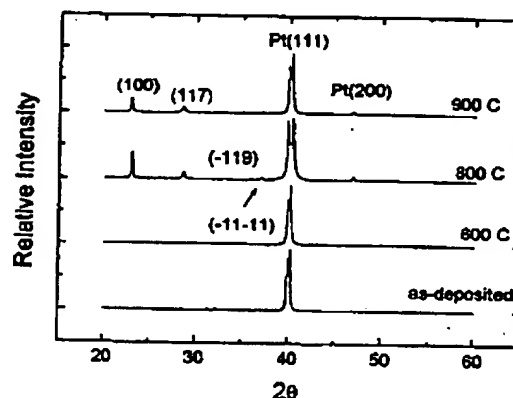


FIG. 4. X-ray diffraction of  $(\text{TiO}_2)_{0.08}-(\text{Ta}_2\text{O}_5)_{0.92}$  films (1100 Å) annealed under various conditions.

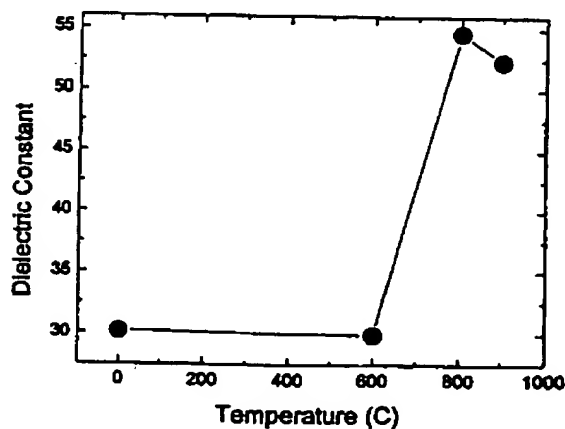


FIG. 5. Dielectric constant of  $(\text{TiO}_2)_{0.08}-(\text{Ta}_2\text{O}_5)_{0.92}$  films as a function of annealing temperature. The measurement was performed at zero bias and 1 MHz. The film thickness is 1100 Å.

incorporation. Since the composition is roughly the same for both film and bulk, it is then obvious that the heat treatment may play an important role in determining the dielectric constant. From the dielectric constant ratio of film to bulk, which is not a constant, the effect of heat treatment is composition dependent too.

To summarize, we have shown that the dielectric constant of  $\text{Ta}_2\text{O}_5$  thin film, like its bulk form, can also be greatly enhanced by adding a small quantity of  $\text{TiO}_2$ . Such an enhancement critically depends on the amount of  $\text{TiO}_2$  incorporated, and also appears on both crystalline and amorphous structures. As compared to the bulk value, the highest dielectric constant of the crystallized film is much smaller. The exact mechanism responsible for the enhancement is yet to be found.

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<sup>4</sup> H. Shinriki and M. Nakata, *IEEE Trans. Electron Devices* **38**, 455 (1991).

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<sup>8</sup> S. C. Sun and T. F. Chen, *Tech. Dig. Int. Electron Devices Meet.*, 333 (1994).